Journal of Ceramic Processing Research. Vol. 13, No. 2, pp. 93~96 (2012)

J O U R N A L O F
Ceramic Processing Research

Low-temperature sintering and microwave dielectric properties of $Mg_4Nb_2O_9$-$CaTiO_3$ composite ceramics with Fe_2O_3-LiF additions

G.G. Yao*, C.J. Pei, H. Ma, H.L. Zhang and X.L. Tian
School of Science, Xi'an University of Posts and Telecommunications, Xi'an 710121, China

The effect of Fe_2O_3-LiF co-doping on the sintering behavior, phase compositions and microwave dielectric properties of $Mg_4Nb_2O_9$-$CaTiO_3$ ceramics were investigated. The Fe_2O_3-LiF addition effectively lowered the sintering temperature of $Mg_4Nb_2O_9$-$CaTiO_3$ ceramics from 1275 °C to 1025 °C. XRD showed the presence of $LiFe_5O_8$ and $Ca(FeTi)_2O_4$ as second phases. With an increase in the sintering temperature, the dielectric constant (ε_r) and quality factor (Q·f) first increase and decrease thereafter, the temperature coefficient of resonant frequency (τ_f) changes slightly. A $Mg_4Nb_2O_9$-$CaTiO_3$ specimen with 0.75 wt% Fe_2O_3-1.5 wt%LiF sintered at 1025 °C/5 h exhibited good microwave dielectric properties: ε_r = 13.6, Q·f = 64 430 GHz (9.5 GHz) and τ_f = –60.4 ppm/K. These properties were correlated with the formation of the second phases, $LiFe_5O_8$ and $Ca(FeTi)_2O_4$.

Key words: Dielectric ceramics, Dielectric properties, Sintering aids.

Introduction

The widespread use of microwave communication has accelerated the search for new technologies to produce miniaturized microwave devices. Recently, considerable attention has been paid to the development of low-temperature cofired ceramic (LTCC) technology for the benefits offered in the fabrication of miniature multilayer devices involving the cofiring of a dielectric and a highly conductive metal, such as silver and copper and various LTCC materials have been explored [1-3]. Moreover, the advanced substrate materials for microwave integrated circuits should have a low dielectric constant (ε_r), a high quality factor (Q·f), and a near-zero temperature coefficient of resonate frequency (τ_f) [4].

$Mg_4Nb_2O_9$, Al_2O_3, $Mg_2V_2O_7$, Li_2MgSiO_4 ceramics have been extensively investigated as potential candidates for advanced ceramic substrate materials [5-8]. In particular, the corundum-like phase $Mg_4Nb_2O_9$ is a suitable material for microwave applications, such as for substrates and resonators at high frequency, because its excellent dielectric properties (ε_r = 12.4, Q·f = 192 000 GHz and τ_f = –70.5 ppm/K) are comparable to those of sintered Al_2O_3 [6]. However, the high sintering temperature (1350 °C-1400 °C) and the large and negative τ_f value limit its application for LTCC microwave devices. Attempts have been made to improve the microwave dielectric properties of the ceramics by preparing various composites, solid solutions and also by doping [9-17]. Among those, Huang *et al.* [16] reported that $Mg_4Nb_2O_9$-$CaTiO_3$ ceramics sintered at 1275 °C showed good microwave dielectric properties of ε_r = 24.8.6, Q·f = 82 200 GHz (9.1 GHz) and τ_f = –0.3 ppm/K, but its sintering temperature was too high for application in LTCC devices. With 3.0 wt% LiF addition, a near-zero τ_f of a $Mg_4Nb_2O_9$-6 wt% $CaTiO_3$ specimen could be sintered at 950 °C by Yokoi *et al.* [15], whereas its Q·f value was reduced to 22 098 GHz. In our previous studies, $Mg_4Nb_2O_9$-$CaTiO_3$ ceramics with 1.7 wt% V_2O_5 could be sintered at as low as 1150 °C while still remaining ε_r = 20, Q·f = 48 000 GHz and τ_f = –12 ppm/K, but the sintering temperature was still high [17]. In order to further reduce the sintering temperature and improve the Q·f of $Mg_4Nb_2O_9$-$CaTiO_3$ composite ceramics, mixtures of Fe_2O_3 and LiF instead of LiF was added in the present research. In this paper, the influence of 0.75 wt%Fe_2O_3-1.5 wt%LiF additions on the sintering behavior, phase compositions and microwave dielectric properties of $Mg_4Nb_2O_9$-$CaTiO_3$ ceramics are investigated.

Experimental

The starting materials are high-purity oxide powders (> 99.9%) : $CaCO_3$, TiO_2, MgO and Nb_2O_5. The powders were separately prepared according to the desired stoichiometry $CaTiO_3$ and $Mg_4Nb_2O_9$, and milled in a nylon jar with agate balls in ethanol for 6 h. The prepared powders were dried then calcined at 1100 °C for 5 h and 1000 °C for 10 h, respectively. The calcined powders were mixed according to the molar fraction $Mg_4Nb_2O_9$-$CaTiO_3$ (MNCT) with Fe_2O_3-LiF additions and then re-milled for 6 h again. The dried powders, with 5 wt% PVA added, were pressed into pellets with 10 mm in diameter and 5 mm in thickness under a pressure of 200 MPa. These pellets were subsequently sintered from 950 to 1050 °C for 5 h with a heating rate of 5 K·minute^{-1}, and then cooled to room temperature.

*Corresponding author:
Tel : +86-29-88166089
Fax: +86-29-88166089
E-mail: yaoguoguang@xupt.edu.cn

The reaction of the calcined powders taking place during heat treatment was investigated by thermal gravimetric and differential thermal analysis (TG-DTA SDTQ600, USA). The densities of the sintered ceramics were measured by Archimede's method. The crystal structures were analyzed by X-ray diffraction (XRD Rigaku D/MAX2550, Japan) using CuK*a* radiation. The microstructure of pellets were investigated using a scanning electron microscope (SEM) (Fei Quanta 200, Holland). The microwave dielectric properties of sintered samples were measured using HP8720ES network analyzer. The temperature coefficients of the resonant frequency were measured in the temperature range of 25-80 °C.

Results and Discussion

Fig. 1 shows the XRD patterns of $Mg_4Nb_2O_9$-$CaTiO_3$ (MNCT) ceramics with 0.75 wt%Fe_2O_3-1.5 wt%LiF additions sintered at different temperatures. It is seen that the pellets sintered at 975 °C were composed of a main phase of $Mg_4Nb_2O_9$, mixed with second phases $LiFe_5O_8$ and $Ca(FeTi)_2O_4$; but the presence of $CaTiO_3$ was not detected. This shows the reaction between Fe_2O_3 and $CaTiO_3$ took place in the sintering process. As the sintering temperature was increased to above 1000 °C, the amount of $Mg_4Nb_2O_9$ phase increased while that of $LiFe_5O_8$ and $Ca(FeTi)_2O_4$ phases decreased. Moreover, some new peaks of $CaTiO_3$ and an unknown crystalline phase were developed.

Fig. 2 illustrates the bulk densities of MNCT ceramics with 0.75 wt%Fe_2O_3-1.5 wt%LiF as a function of the sintering temperature. With an increase in the sintering temperature, the bulk densities increased gradually, and then saturated at 1000 °C. The variation of the bulk density could be explained by the changes in the microstructure as discussed later. In addition, the densification sintering temperature of MNCT ceramics with 0.75 wt%Fe_2O_3-1.5 wt%LiF is obviously lower than reported by Huang *et al*. [16] for a MNCT specimen, which indicates that the Fe_2O_3-LiF is an effective sintering aids for MNCT ceramics.

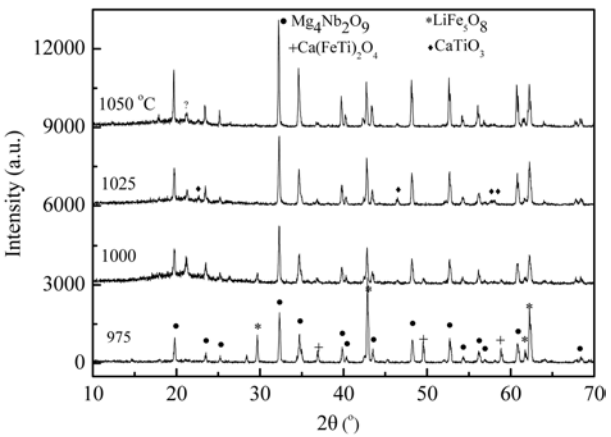

Fig. 1. XRD patterns of MNCT ceramics with 0.75 wt%Fe_2O_3-1.5 wt%LiF sintered at different temperatures.

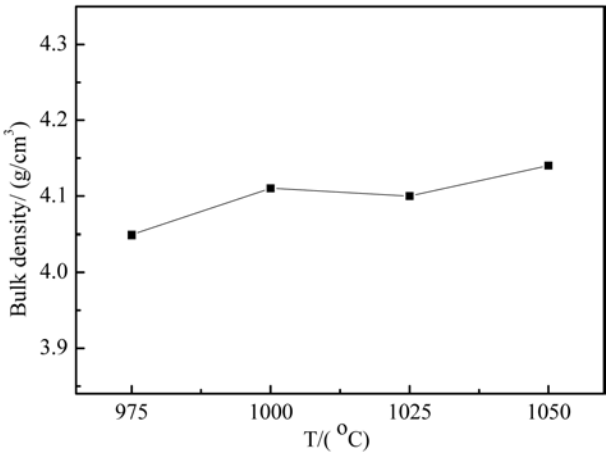

Fig. 2. Bulk density of MNCT ceramics with 0.75 wt%Fe_2O_3-1.5 wt%LiF additions as a function of sintering temperature.

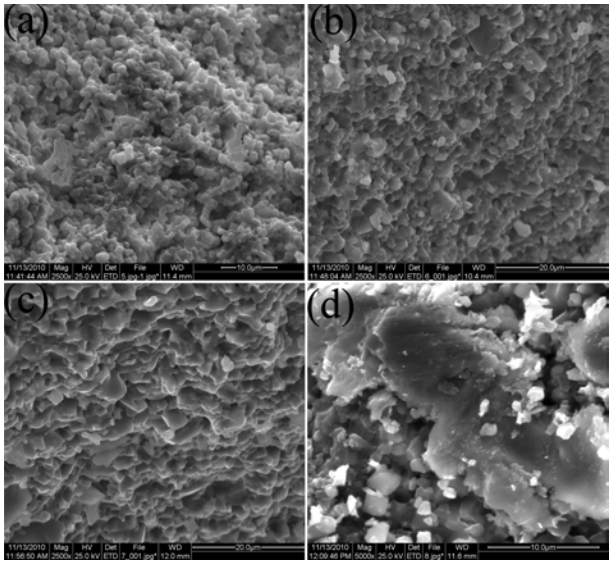

Fig. 3. SEM images of the fractured surfaces of MNCT ceramics with 0.75 wt%Fe_2O_3-1.5 wt%LiF additions sintered at various temperature: (a) 975 °C, (b) 1000 °C, (c) 1025 °C and (d) 1050 °C.

The Typical SEM images of the fractured surfaces of MNCT ceramics with 0.75 wt%Fe_2O_3-1.5 wt%LiF additions sintered at different temperatures are given in Fig. 3. It can be seen that the porosity decreased with an increase in the sintering temperature, which is in accord with the changes of bulk density as described above. A dense microstructure of MNCT ceramics with 0.75 wt%Fe_2O_3-1.5 wt%LiF sintered at 1025 °C with only few pores existing was developed, as shown in Fig. 3(c). The average grain size is about 1-3 um, which is much smaller than for pure MNCT ceramics [16]. This result indicates that the addition of Fe_2O_3-LiF effectively accelerated the sintering process, lowered the sintering temperature, and helped to obtain a small grain size. However, for the specimen sintered at 1050 °C, abnormal grain growth and the effect of a large amount of liquid phase can be observed, which would damage its microwave dielectric properties.

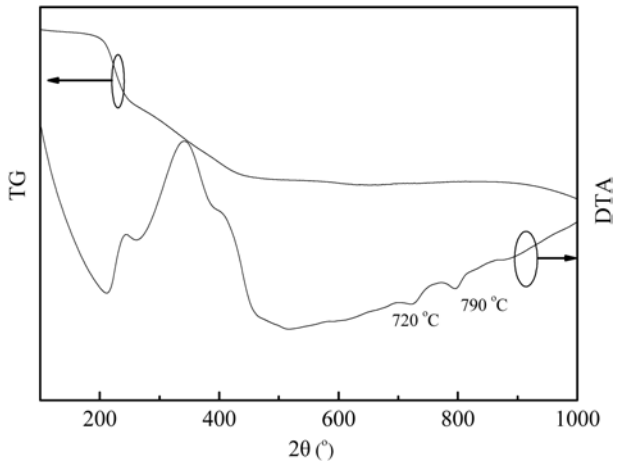

Fig. 4. TG - DTA curves of MNCT calcined powders doped with 0.75 wt%Fe_2O_3-1.5 wt%LiF.

In order to evaluate the sintering behavior of the composite ceramics, DTA-TG analyses were performed on MNCT powders doped with 0.75 wt%Fe_2O_3-1.5 wt%LiF, as shown in Fig. 4. In the temperature range from room temperature to 500 °C, the TG curve showed a distinct weight loss. Meanwhile, two exothermic peaks were observed in the DTA curve, which were related to the weight loss. These exothermic peaks are considered to be caused by the combustion of the organic binders [18]. Moreover, two distinct endothermic peaks were observed in the temperature range of 700-800 °C. The endothermic peaks are attributed to the eutectic reaction in the Li_2O-Fe_2O_3 system, according to the phase diagram [19], which was responsible for the low-temperature densification of MNCT ceramics here. There might be a liquid sintering mechanism for this system.

The microwave dielectric properties of MNCT ceramics with 0.75 wt%Fe_2O_3-1.5 wt%LiF additions sintered at various temperatures are presented in Fig. 5. The dielectric constant shows the same tendency as the bulk density. A saturated ε_r value of 13.6 was obtained for the specimen sintered at 1025 °C for 5 h. The ε_r of the MNCT ceramics with 0.75 wt%Fe_2O_3-1.5 wt%LiF is lower than that of un-doped MNCT ceramics [16], which might be connected with the second phases $LiFe_5O_8$ and $Ca(FeTi)_2O_4$. The $Q{\cdot}f$ values increased and reached a maximum value and then decreased as the sintering temperature was increased. There are several factors that contribute to the dielectric loss at microwave frequencies, such as density, porosity, second phases, grain boundaries, and inclusions in real homogeneous ceramics [20]. The increase of $Q{\cdot}f$ is attributed to an increase in the density, whereas its decrease is attributed to the abnormal grain growth combined with the presence of a large amount of liquid phase as shown in Fig. 3(d). Moreover, the τ_f value is almost independent of the sintering temperature and remains between –58 and –61 ppm/K, but it is deteriorated compared with pure MNCT ceramics [16], as shown in Fig. 5(b). Although there is no relevant report on the dielectric properties of

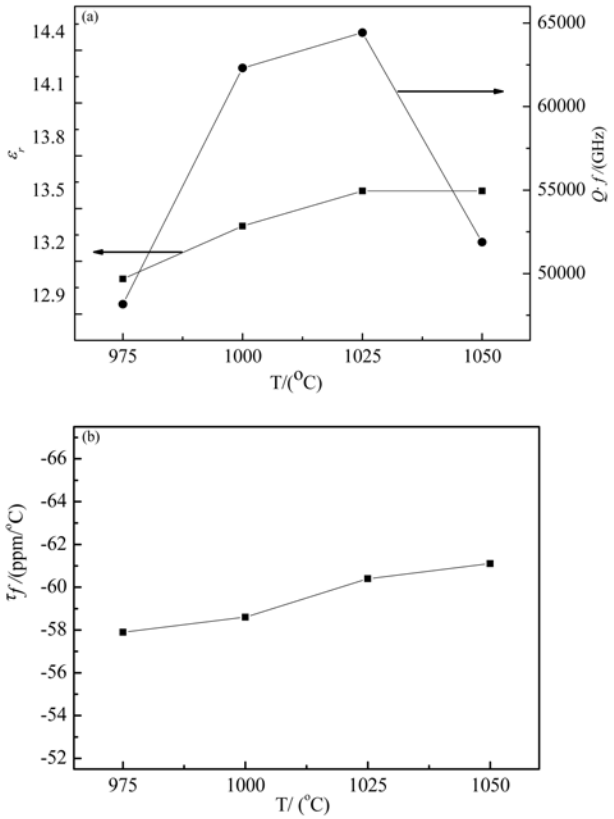

Fig. 5. Variation of microwave dielectric properties of MNCT ceramics with 0.75 wt%Fe_2O_3-1.5 wt%LiF additions versus the firing temperature: (a) ε_r , $Q{\cdot}f$ and (b) τ_f.

$LiFe_5O_8$ and $Ca(FeTi)_2O_4$ phases, from our experimental results, we can conclude that the $LiFe_5O_8$ and $Ca(FeTi)_2O_4$ phases might have a larger negative τ_f than that of $CaTiO_3$ [21] As a result, the MNCT ceramic with 0.75 wt%Fe_2O_3-1.5 wt%LiF sintered at 1025 °C exhibits good microwave dielectric properties of ε_r = 13.6, $Q{\cdot}f$ = 64 430 GHz (9.5 GHz) and τ_f = –60.4 ppm/K.

Conclusion

The sintering temperature of $Mg_4Nb_2O_9$-$CaTiO_3$ ceramics is significantly lowered to 1025 °C by the addition of 0.75 wt%Fe_2O_3-1.5 wt%LiF due to a liquid effect. $LiFe_5O_8$ and $Ca(FeTi)_2O_4$ as impurity phases were developed in the $Mg_4Nb_2O_9$-$CaTiO_3$ ceramics with the addition of Fe_2O_3-LiF. It is considered that the microwave dielectric properties of the ceramics are closely related to the impurity phase. With an increase in the sintering temperature, the dielectric constant and quality factor first increase and decrease thereafter, the temperature coefficient of the resonant frequency changes slightly. The specimens sintered at 1025 °C for 5 h possess ε_r of 13.6, $Q{\cdot}f$ of 64 430 GHz (9.5 GHz) and τ_f of –60.4 ppm/K.

Acknowledgements

This work was supported by the Nature Science

Fundation of Shaan xi Province (No. 2009JM6001), and Shaan xi Province Department Education (No. 11JK0829).

References

1. K.M. Manu, P.S. Anjana and M.T. Sebastian, Mater. Lett. 65 (2011) 565-567.
2. D. Zhou, C.A. Randall, H. Wang and X. Yao, J. AM. Ceram. Soc. 93 (2010) 2147-2150.
3. H. Zhuang, Z.X Yue, F. Zhao and L.T Li, J. Alloys. Compd. 472 (2009) 411-415.
4. S. Kim, M.E. Song and S. Nahm, J. AM. Ceram. Soc. 91 (2010) 4133-4136.
5. H. Ogawa, A. Kan, S. Ishihara and Y. Higashida, J. Eur. Ceram. Soc. 23 (2004) 2485-2488.
6. N.M. Alford and S.J. Penn, J. Appl. Phys. 80 (1996) 5895-5898.
7. M.R. Joung, J.S. Kim, M.E. Song and Sahn Nahm, J. AM. Ceram. Soc. 93 (2010) 2132-2135.
8. S. George, P.S. Anjana and M.T. Sebastian. J. AM. Ceram. Soc. 92 (2009) 1244-1249.
9. K. Akinori and O. Hirotaka, Jpn. J. Appl. Phys. 42 (2003) 6154-6158.
10. A. Kan, H. Ogawa, A.Yokoi, Mater. Res. Bull. 41 (2006) 1178-1184.
11. A. Kan, H. Ogawa and A.Yokoi, J. Eur. Ceram. Soc. 27 (2007) 2977-2979.
12. A. Yoshida, H. Ogawa and A. Kan, J. Eur. Ceram. Soc. 24 (2004) 1765-1768.
13. C.L. Huang and W.R. Yang, J. Alloys. Compd. 509 (2011) 2269-2272.
14. C.L. Huang, W.R. Yang and Y.R. Chen, J. Alloys. Compd. 495 (2010) L5-L7.
15. A. Yokoi, H. Ogawa, A. Kan and H. Ohsato, J. Eur. Ceram. Soc. 25 (2005) 2871-2875.
16. C.L. Huang, J.Y. Chen and C.C. Liang, J. Alloys. Compd. 44 (2009) 1111-1115.
17. G.G. Yao and P. Liu, Phy. B. 405 (2010) 547-551.
18. T.H. Fang, Y.J. Hsiao and L.W. Ji, J. Cryst. Growth. 310 (2008) 3331-3334.
19. D.W. Strickler and R. Roy, J. AM. Ceram. Soc. 44 (1961) 225-230.
20. S.J. Penn, N.M. Alford and K. Schrape, J. AM. Ceram. Soc. 80 (1997) 1885-1888.
21. R.C. Kell, A.C. Greenham, J. Am. Ceram. Soc. 56 (1973) 352-354.